

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
27 December 2001 (27.12.2001)

PCT

(10) International Publication Number
WO 01/97973 A1

(51) International Patent Classification⁷: **B01J 39/20**,
41/14, 45/00, C03C 25/26, 25/28, 25/30

(21) International Application Number: PCT/US01/19952

(22) International Filing Date: 20 June 2001 (20.06.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/599,811 21 June 2000 (21.06.2000) US

(71) Applicant: **BOARD OF TRUSTEES OF UNIVERSITY OF ILLINOIS** [US/US]; 352 Henry Administration Building, 506 S. Wright, Urbana, IL 61801 (US).

(72) Inventors: **ECONOMY, James**; 105 Whitehall Court, Urbana, IL 61801 (US). **DOMINGUEZ, Lourdes**; 713 South Walnut, Urbana, IL 61801 (US). **BENAK, Kelly**; 2901 Heritage Drive, Champaigne, IL 61822 (US).

(74) Agent: **RAUCH, Paul, E.**; Brinks Hofer Gilson & Lione, P.O. Box 10087, Chicago, IL 60610 (US).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: POLYMERIC ION EXCHANGE FIBERS

(57) Abstract: Ion exchange resin composite fibers include a substrate fiber, and an ion exchange resin, on the substrate fiber. The ion exchange resin composite fibers exhibit greatly increased kinetic rates of reaction and regeneration.



WO 01/97973 A1

-1-

TITLE

POLYMERIC ION EXCHANGE FIBERS

FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

5 The subject matter of this application was in part funded by the National Science Foundation (Grant no. DMR-97-12489; UFAS No. 1-5-31414). The government may have certain rights in this invention.

BACKGROUND

The present invention relates to ion exchange materials.

10 Ion exchange materials have been used for purification and demineralization. These materials have a three-dimensional network to which ions are attached. In ion exchange resins, the three-dimensional network is a polymer. In carbon ion exchangers, the three-dimensional network is activated carbon.

15 Ion exchange resins have been known for almost sixty years ("Ion Exchangers"; Dorfner, K. (Ann Arbor Science Publishers, Inc.1972)). The three-dimensional network helps preserve the structural integrity of the material, usually in the form of beads, while the ions provide exchange sites. A large variety of ion exchange resins are described in "Encyclopedia of Chemical Technology" Kirk-Othmer, 3rd ed., vol. 13, pp. 685-93 (1981); and 20 "Ion Exchangers" ed. Konrad Dorfner, pp. 28-44, and pp. 206-84 (Walter de Gruyter, 1991).

25 These materials suffer from a number of disadvantages. During the activation of the resin (the stage of attachment of the ions), solvent must be used to pre-swell the cross-linked resin, to reduce the effects of osmotic shock. Furthermore, the beads are very susceptible to fracture and breakage and must be kept wet at all times. Also, pre-swelling prior to service is often required, increasing shipping costs. Finally, there is also a need for ion exchange resins having higher contact efficiencies, speed of regeneration, and longer service life.

-2-

Glass or mineral fibers, coated with activated carbon, have been prepared. These materials are described in U.S. patent no. 5,834,114. Glass or mineral fibers coated with activated carbon are described as being prepared by coating a glass or mineral fiber substrate with a resin, cross-linking the resin, heating the coated fiber substrate and resin to carbonize the resin, and exposing the coated fiber substrate to an etchant to activate the coated fiber substrate.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph showing the capacities resulting from varied sulfonation treatments of samples and comparative samples; and

Figure 2 is a graph showing batch rates of exchange at varying saline concentrations of samples and comparative samples.

BRIEF SUMMARY

In a first aspect, the present invention includes a composite, containing (i) a substrate fiber, and (ii) an ion exchange resin, on the substrate fiber.

In a second aspect, the present invention includes a method of making a composite, including forming an ion exchange resin from a resin. The resin is on a substrate fiber.

The term "ion exchange resin" means a resin that contains an ionic group, thus allowing the material to exchange ions with a solvent, but also means a resin that contains groups capable of chelating ions.

DETAILED DESCRIPTION

The ion exchange resin composite fibers exhibit greatly increased kinetic rates of reaction and regeneration, as compared with commercially available ion exchange resins in the form of beads. Furthermore, the strength is increased by the substrate fiber, reducing fracture and breakage, and allowing a larger variety of forms to be produced. In addition, the thickness of the ion exchange resin on the composite may be very thin, providing excellent kinetics, and preferably the need for solvents for activation or prior to end-use

-3-

may be eliminated, while thicker coatings may provide much higher capacities.

The substrate fiber may include any material that can tolerate the conditions necessary to form the structure. Examples include natural fibers, HEPA filters, e-glass fibers, synthetic fibers used in clothing, polyesters, polyethylene, polyethylene terephthalate, nylon 6, nylon 66, polypropylene, KEVLAR™, liquid crystalline polyesters, and syndiotactic polystyrene. Other examples include natural and synthetic fibers, for example: glass fibers; mineral fibers such as asbestos and basalt; ceramic fibers such as TiO₂, SiC, and BN; metal fibers such as iron, nickel and platinum; polymer fibers such as TYVEK™; natural fibers such as cellulose and animal hair; and combinations thereof. Some preferred substrate fibers are listed in the table below.

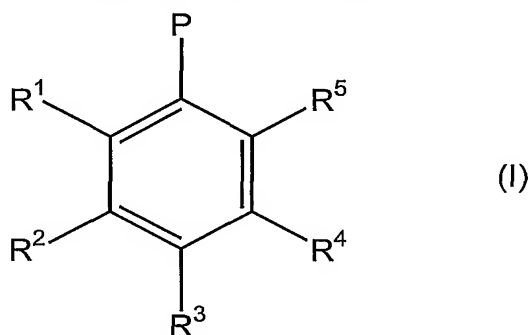
Company	Product Line	Description
CRANE & CO.	Crane 230 (6.5μm) Crane 232 (7.5μm)	Non-woven Fiber Glass Mats Non-woven Fiber Glass Mats
FIBRE GLAST	519 (0.75 oz.) 573 (9 oz.)	wovens wovens
HOLLINGSWORTH & VOSE	BG05095 HE1021	glass paper or felts
JOHNS MANVILLE	DURAGLASS® 7529 (11μm)	non-woven fiber glass mats
LYDALL MANNING	MANNIGLAS®	non-woven fiber glass mats
DUPONT	TYVEK®	HDPE Spun bonded paper

The ion exchange resin composite fibers may be present in any form. Examples include loose fibers, woven and non-woven fabrics, papers, felts and mats. The ion exchange resin composite fibers may be made from substrate fibers already present in a specific form, or the ion exchange resin composite fibers may first be prepared from loose substrate fibers, and made into the specific form. Furthermore, the ionic exchange resin may itself be used as an adhesive to hold the fibers together.

Any ion exchange resin may be used in the ion exchange resin composite fibers. A large variety of ion exchange resins are described in "Encyclopedia of Chemical Technology" Kirk-Othmer, 3rd ed., vol. 13, pp.

-4-

685-93 (1981); and "Ion Exchangers" ed. Konrad Dorfner, pp. 28-44, and pp. 206-84 (Walter de Gruyter, 1991), both of which are hereby incorporated by reference. Examples include polystyrenes such as polystyrene cross-linked with divinylbenzene, copolymers of methacrylate and styrene cross-linked with divinylbenzene, each also containing ionic or chelating groups; polyvinylpyridines; and poly(meth)acrylic acids such as polymethacrylic acid cross-linked with divinylbenzene, which may contain additional ionic or chelating groups. Preferably, the resin is a cross-linked polymer comprising phenyl groups, for example a polymer containing groups of the formula (I):



where P indicates where the group of formula (I) is attached to the polymer, and R^1 , R^2 , R^3 , R^4 , R^5 are each independently selected from H, halo, C_1 - C_{10} alkyl, C_1 - C_{10} haloalkyl, C_1 - C_{10} alkenyl, an ionic group and a chelating group, where at least one of R^1 , R^2 , R^3 , R^4 , R^5 is an ionic group or a chelating group. Examples of ionic groups are anionic groups such as $-SO_3^-$, $-COO^-$, $-PO_3^-$ and $AsO_3(H)^-$; and cationic groups such as trialkyl ammonium groups, $-(R^1)_3N^+$, where each R^1 is independently an alkyl group (i.e. methyl, ethyl, propyl, butyl, etc.). Examples of chelating groups include hydroxyl, amino, iminodiacetate groups and thiol groups. Mixtures of different anionic groups, or cationic groups, or chelating groups are possible, as well as mixtures of anionic, cationic and/or chelating groups.

The length of the ion exchange resin composite fibers are not limited, and may be, for example, 0.01 mm to 100 m in length. The ion exchange resin composite fibers may be prepared from longer substrate fibers, then cut or chopped. Furthermore, the diameter of the ion exchange resin composite

fibers are also not limited, and may be, for example 100 Å to 1 mm in diameter. Preferably, the fibers have an aspect ratio of at least 10.

The ion exchange resin of the ion exchange resin composite fibers may be present on isolated regions on the surface of the substrate fibers, may completely enclose the substrate fibers, or enclose all of the substrate fibers except the ends of the substrate fibers. For example, if the substrate fibers were completely enclosed by the ion exchange resin, then chopping would result in the ends of the fibers being exposed.

The weight ratio between the ion exchange resin and the substrate fibers in the ion exchange resin composite fibers is not limited, but does affect final properties. For example, if the amount of ion exchange resin is very large compared to the amount of substrate fibers, then the brittleness of the ion exchange resin may reduce the flexibility of the ion exchange resin composite fibers. Preferably, the ion exchange resin composite fibers include 10 to 90% by weight of ion exchange resin, more preferably 20 to 80% by weight of ion exchange resin, including 30%, 40%, 50%, 60%, and 70% by weight of ion exchange resin.

The ion exchange resin composite fibers may be prepared by coating the substrate fibers with a resin, and then converting the resin into an ion exchange resin, by introducing ionic and/or chelating groups by chemical reaction with modifying agents. Examples of resins include polystyrenes such as polystyrene cross-linked with divinylbenzene and copolymers of methacrylate and styrene cross-linked with divinylbenzene; poly (vinylbenzyl halides) such as poly (vinylbenzyl chloride) cross-linked with divinylbenzene; and poly(meth)acrylates such as polymethacrylate cross-linked with divinylbenzene. The resin may contain phenyl groups.

One method to coat the resin on the substrate fibers is to start the formation of the resin by polymerizing monomers, stop the polymerization before the polymerizing mixture becomes a gel, coat the fibers with the mixture, and then complete the polymerization. The viscosity of the polymerizing mixture can be adjusted with a solvent, so that the thickness of the coating on the fibers can be easily controlled.

-6-

In a second method, a first polymer can be formed, which is then dissolved into a solvent. Optionally, a cross-linking agent could be added to this mixture. The mixture is coated onto the fibers, and then the solvent is removed. The polymer is then cross-linked, for example by exposure to a cross-linking agent, by exposure to radiation, or activation of the optionally added cross-linking agent. The coated fibers, either before or after cross-linking, may be made into a different form, such as a mat, using the resin as an adhesive to hold the coated fibers together, for example by pressing the coated fibers together while heating.

In a third method, a resin is melted, and the melt is coated onto the fibers. Optionally, the resin may be exposed to a cross-linking agent, or exposed to radiation. Furthermore, the coated fibers may be made into a different form, such as a mat, using the resin as an adhesive to hold the coated fibers together, for example by pressing the coated fibers together while heating.

Any method may be used to coat the fibers, including dip coating and spray coating.

An activating agent is used to form ionic or chelating groups in the resin, to form the ion exchange resin. The selection of activating agent depends on the group in the resin where the ionic group or chelating group will be formed, as well as which ionic or chelating group is desired. In the case of polystyrene, the ionic groups may be attached to phenyl groups in the polymer, such as by reaction with sulfuric acid (to attach sulfonyl groups) or in the case of poly(vinylbenzyl chloride), with trimethyl amine (to attach trialkyl ammonium groups). In the case of poly(meth)acrylates, the acid groups may be formed by saponification of the esters, by reaction with an acid. Preferably no solvent is used during the activation process, because swelling caused by the solvent may result in delamination of the resin from the fiber.

EXAMPLES

-7-

The following examples and preparations are provided merely to further illustrate the invention. The scope of the invention is not construed as merely consisting of the following examples.

5

Example 1. Polymerization and activation of cationic resin coated glass fibers

I. Polymerization:

10

A copolymer of styrene, 8% wt. divinylbenzene (80% mixture of m, p isomers and >17% ethylvinylbenzene, and <1% o, m, p diethylbenzene), and benzoyl peroxide initiator, were rigorously mixed and heated at 80 to 85 °C for approximately 17 to 24 minutes, or just before the gel point, and subsequently quenched in an ice bath, to form the oligomer. The fiberglass substrate

15

CRANE 230 (6.5 μ m fiber diameter) was then coated with the oligomer. The fibers were then turned occasionally to avoid pooling while sitting in air for one hour. The coated glass samples were cured at 85°C in a Lindberg furnace under nitrogen for 4 hours. Following this procedure, a resin loading of 60 - 65% by weight was achieved.

20

II. Functionalization:

The resin-coated fibers were treated with 150-ml concentrated sulfuric acid for four hours at 85°C with 1% silver sulfate as a catalyst under stirring. After activation, the samples were treated to a stepped-dilution rinse (50%,

25

25%, 12%, 6%, and 3% sulfuric acid rinse). Finally, the resin-coated fibers were rinsed with pure de-ionized water until all excess acid had been removed.

Example 2. Polymerization and activation of cationic resin coated glass fibers

30

I. Polymerization:

Same as Example 1

II. Functionalization:

The resin-coated fibers were treated with 150-ml concentrated sulfuric acid for twelve hours at 25°C with 1% silver sulfate as a catalyst under stirring. After activation, the samples were treated to a stepped-dilution rinse (50%, 25%, 12%, 6%, and 3% sulfuric acid rinse). Finally, the resin-coated fibers were rinsed with pure de-ionized water until all excess acid had been removed.

Example 3. Polymerization and activation of cationic resin coated glass fibers

I. Polymerization:

A copolymer of styrene, 5 wt.% divinylbenzene (80% mixture of m, p isomers and >17% ethylvinylbenzene, and <1% o, m, p diethylbenzene), and benzoyl peroxide initiator were rigorously mixed and heated at 80 to 85 °C for approximately 17 to 24 minutes, or just before the gel point, and subsequently quenched in an ice bath, to form the oligomer. The fiberglass substrate CRANE 230 (6.5 µm fiber diameter) was then coated with the oligomer. The fibers were then turned occasionally to avoid pooling while sitting in air for one hour. The coated glass samples were cured at 85°C in a Lindberg furnace under nitrogen for 4 hours. Following this procedure, a resin loading of 60 - 65% by weight is achieved.

II. Functionalization:

Same as Example 1

Example 4. Polymerization and activation of anionic resin coated glass fibers

I. Polymerization:

A copolymer of vinylbenzyl chloride, 8 wt.% divinylbenzene (80% mixture of m, p isomers and >17% ethylvinylbenzene, and <1% o, m, p diethylbenzene) were rigorously mixed with benzoyl peroxide initiator and

-9-

heated at 80 to 85 °C for approximately 17 to 24 minutes, or just before the gel point, and subsequently quenched in an ice bath. The fiberglass substrate CRANE 230 (6.5 μ m fiber diameter) was then coated with the oligomer. The fibers were then turned occasionally to avoid pooling while sitting in air for four hours. Excess monomer must be removed with a paper towel or other adsorbent. The coated glass samples were cured at 85°C in a Lindberg furnace under nitrogen for 4 hours. Following this procedure, a resin loading of 80 - 90% by weight is achieved.

II. Functionalization:

The resin-coated fibers were treated with ~ 50 ml of trimethylamine for 45 minutes at 25°C. After activation, the samples were rinsed with approximately 200 ml of 2N HCl. Finally, the resin-coated fibers were rinsed with pure de-ionized water and placed in a vacuum furnace overnight at 65°C to dry.

Example 5. Polymerization and activation of anionic resin coated glass fibers

I. Polymerization:

Same as Example 1

II. Functionalization:

The resin-coated fibers were treated with ~ 50 ml of trimethylamine for 20 minutes at 45°C. After activation, the samples were rinsed with approximately 200 ml of 2N HCl. Finally, the resin-coated fibers were rinsed with pure de-ionized water and placed in a vacuum furnace overnight at 65°C to dry.

Example 6. Polymerization and activation of anionic resin coated glass fibers

I. Polymerization:

-10-

A copolymer of vinylbenzyl chloride, 5% wt. divinylbenzene (80% mixture of m, p isomers and >17% ethylvinylbenzene, and <1% o, m, p diethylbenzene) were rigorously mixed with benzoyl peroxide initiator and heated at 80 to 85 °C for approximately 17 to 24 minutes, or just before the gel point, and subsequently quenched in an ice bath, to form the oligomer. The fiberglass substrate Crane 230 (6.5 µm fiber diameter) was then coated with the oligomer. The fibers were then turned occasionally to avoid pooling while sitting in air for four hours. Excess monomer was removed with a paper towel or other adsorbent. The coated glass samples were cured at 85°C in a Lindberg furnace under nitrogen for 4 hours. Following this procedure, a resin loading of 80 - 90% by weight is achieved.

II. Functionalization:

Same as Example 1.

Batch Capacity Experiments

The cation capacity was determined in a conventional manner. In a 150-ml beaker was added 50 ml of 1M sodium chloride solution (excess), < 0.5-g sample of dry resin coated fibers, and two drops of phenolphthalein indicator. The contents were stirred and titrated with standard 0.1-M sodium hydroxide solution. The volume of sodium hydroxide used, times the normality per gram of exchange material, is representative of the normalized loading capacity in meq/g units. The results are shown Figure 1. The samples were prepared in the same was as Example 1, except that the time of sulfonation and/or temperature of sulfonation was varied as indicated in the figure.

Regeneration Studies

After each capacity run, samples were regenerated with a solution of 2N HCl acid, rinsed thoroughly with deionized water and thoroughly dried overnight. After each cycle, samples were weighed directly after drying to keep water adsorption to a minimum for capacity measurements. These

-11-

systems were successfully regenerated for up to ten times with little to no observable weight loss or loss in activity.

Kinetics Studies

5 Batch kinetic tests for the polymeric coated glass fibers of Examples 1 were conducted with saline solutions of varying concentrations (0.01M and 0.005 M NaCl). The samples were vacuum dried at 62°C. After weighing, the resin coated fibers were tested bone dry. Exactly 50 ml of 0.05-M sodium chloride solution was placed in a 150-ml beaker with two drops of
10 phenolphthalein indicator, and 1ml of standard sodium hydroxide. While stirring, a known mass of dry resin-coated fabric was added and the time required to discharge the indicator (neutralize the solution) was noted. This step was repeated until the indicator no longer discharged. The comparative polymeric beads were from Purolite - Type C-150H. The results are shown in
15 Figure 2.

 Obviously, numerous modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may
20 be practiced otherwise than as specifically described herein.

CLAIMS

1. A composite, comprising:
 - (i) substrate fibers, and
 - (ii) an ion exchange resin, on said substrate fibers.
- 5 2. The composite of Claim 1, wherein said ion exchange resin comprises phenyl groups.
3. The composite of Claim 1, wherein said substrate fibers comprises a member selected from the group consisting of glass, polymer, and mixtures there of.
- 10 4. The composite of Claim 1, wherein said ion exchange resin comprises ionic groups.
5. The composite of Claim 1, wherein said ion exchange resin comprises chelating groups.
- 15 6. The composite of Claim 1, wherein said substrate fibers are in the form of one member selected from the group consisting of fabrics, papers, felts and mats.
7. The composite of Claim 4, wherein said ionic groups are selected from the group consisting of sulfonic groups and trialkyl ammonium groups.
- 20 8. The composite of Claim 4, wherein said ion exchange resin comprises polystyrene cross-linked with divinylbenzene.
9. The composite of Claim 8, wherein said substrate fibers comprise glass.
- 25 10. A method of making a composite, comprising:
 - forming an ion exchange resin from a resin;
 - wherein said resin is on substrate fibers.

-13-

11. The method of Claim 10, further comprising, prior to said forming, coating said resin on said substrate fibers.

12. The method of Claim 10, wherein said forming comprises reacting said resin with an activating agent.

5 13. The method of Claim 12, wherein said resin comprises phenyl groups.

14. The method of Claim 13, wherein said activating agent is selected from the group consisting of sulfuric acid and trimethyl amine.

10 15. The method of Claim 10, wherein said substrate fibers comprise a member selected from the group consisting of glass, polymer, and mixtures there of.

16. The method of Claim 10, wherein said substrate fibers are in the form of one member selected from the group consisting of fabrics, papers, felts and mats.

15 17. The method of Claim 10, wherein said resin comprises polystyrene cross-linked with divinylbenzene.

18. The method of Claim 17, wherein said substrate fibers comprise glass.

20 19. The method of Claim 18, wherein said forming comprises reacting said resin with an activating agent selected from the group consisting of sulfuric acid and trimethyl amine.

20. A composite, prepared by the method of Claim 10.

21. A composite, prepared by the method of Claim 12.

22. A composite, prepared by the method of Claim 14.

25 23. A composite, prepared by the method of Claim 17.

-14-

24. A composite, prepared by the method of Claim 18.
25. A composite, prepared by the method of Claim 19.
26. A method of purifying a liquid, comprising:
contacting a liquid with the composite of Claim 1.
27. A method of purifying a liquid, comprising:
contacting a liquid with the composite of Claim 6.
28. A method of purifying a liquid, comprising:
contacting a liquid with the composite of Claim 20.

5

10

15

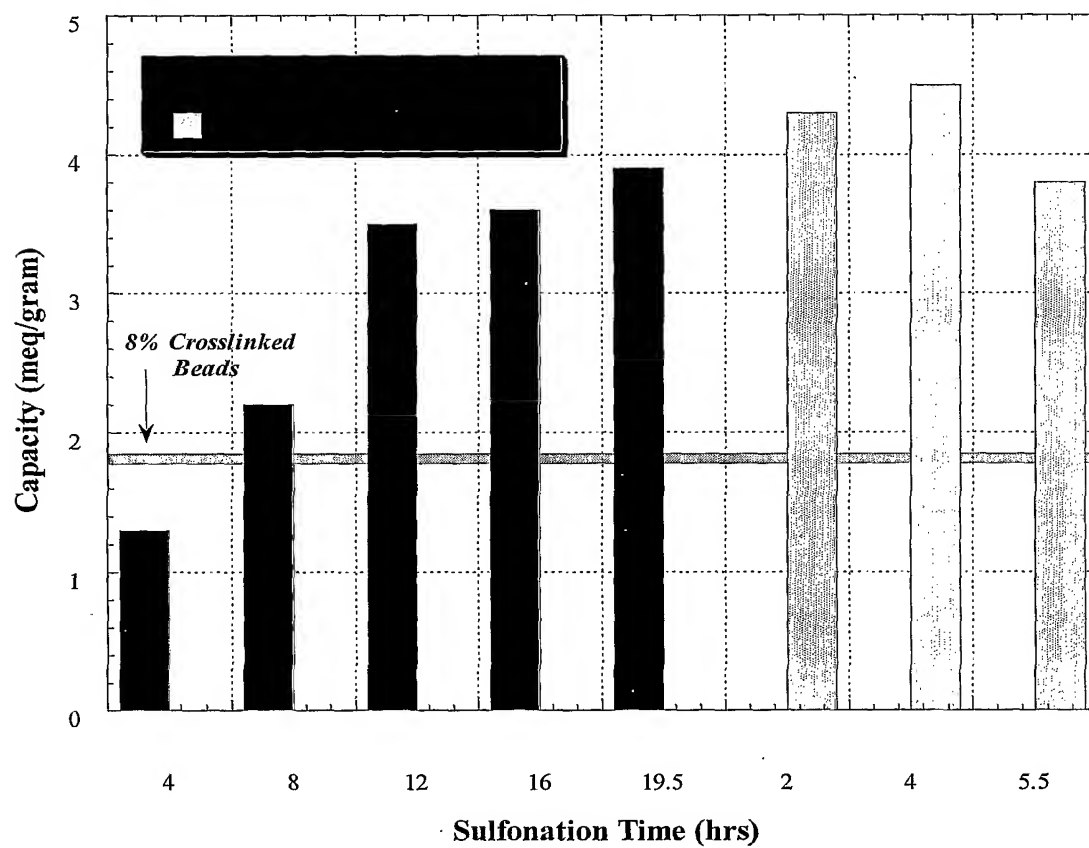
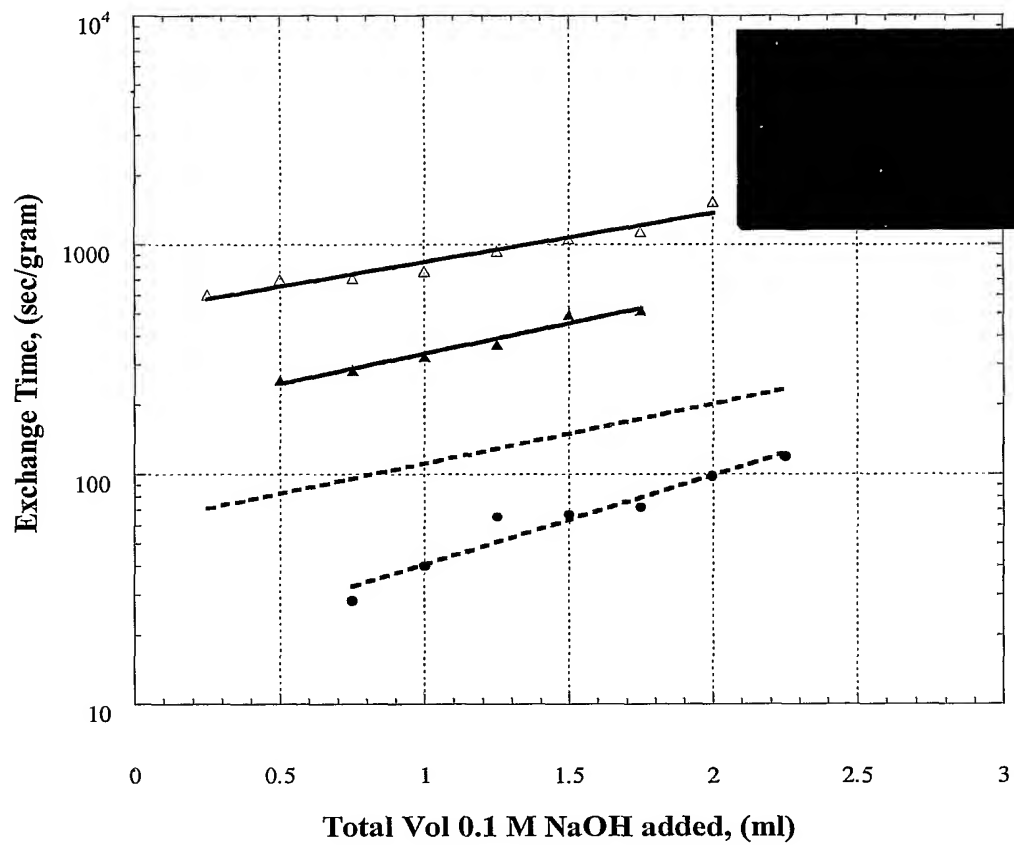
Figure 1: Capacities Resulting from Varied Sulfonation Treatments

Figure 2: Batch Rates of Exchange at Varying Saline Concentration

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/19952

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01J39/20 B01J41/14 B01J45/00 C03C25/26 C03C25/28
C03C25/30

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01J C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 318 846 A (BRUENING RONALD L ET AL) 7 June 1994 (1994-06-07) the whole document ---	1-28
Y	EP 0 630 685 A (INST TEXTILE DE FRANCE) 28 December 1994 (1994-12-28) claims ---	1-4, 6-28
Y	US 5 350 523 A (TOMOI MASAO ET AL) 27 September 1994 (1994-09-27) claims ---	1-4, 6-28
Y	EP 0 036 584 A (RIEDEL DE HAEN AG) 30 September 1981 (1981-09-30) page 1, line 1 -page 5, last paragraph --- -/--	1, 5, 10-13, 15-21, 23-28

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

* & * document member of the same patent family

Date of the actual completion of the international search

7 November 2001

Date of mailing of the international search report

14/11/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Reedijk, A

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/19952

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 547 760 A (TARBET BRYON J ET AL) 20 August 1996 (1996-08-20) column 2, line 6 -column 3, line 38 ---	1,5, 10-13, 15-21, 23-28
A	EP 0 045 824 A (TOKYO ORGAN CHEM IND) 17 February 1982 (1982-02-17) the whole document -----	1-28

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.

PCT/US 01/19952

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5318846	A	07-06-1994	US 5190661 A	02-03-1993
			US 5446182 A	29-08-1995
			AT 175133 T	15-01-1999
			AU 661917 B2	10-08-1995
			AU 4530593 A	04-01-1994
			BR 9306504 A	15-09-1998
			CA 2136635 A1	23-12-1993
			CN 1090794 A ,B	17-08-1994
			CN 1152477 A	25-06-1997
			DE 69322864 D1	11-02-1999
			DE 69322864 T2	27-05-1999
			EP 0644799 A1	29-03-1995
			ES 2128430 T3	16-05-1999
			FI 945746 A	07-12-1994
			HU 69074 A2	28-08-1995
			JP 8500766 T	30-01-1996
			MX 9303429 A1	01-12-1993
			NO 944702 A	06-12-1994
			PL 171797 B1	30-06-1997
			RU 2116828 C1	10-08-1998
			WO 9325306 A1	23-12-1993
			ZA 9304034 A	06-01-1994
EP 0630685	A	28-12-1994	FR 2708273 A1	03-02-1995
			AT 176875 T	15-03-1999
			CA 2126584 A1	29-12-1994
			DE 69416618 D1	01-04-1999
			DE 69416618 T2	09-09-1999
			EP 0630685 A1	28-12-1994
			ES 2131180 T3	16-07-1999
US 5350523	A	27-09-1994	JP 3147389 B2	19-03-2001
			JP 4349941 A	04-12-1992
			JP 3147945 B2	19-03-2001
			JP 5057200 A	09-03-1993
			DE 69119268 D1	13-06-1996
			DE 69119268 T2	31-10-1996
			EP 0444643 A2	04-09-1991
			JP 2001089523 A	03-04-2001
EP 0036584	A	30-09-1981	DE 3011393 A1	01-10-1981
			EP 0036584 A2	30-09-1981
			JP 57007262 A	14-01-1982
US 5547760	A	20-08-1996	AU 686796 B2	12-02-1998
			AU 2295295 A	16-11-1995
			BR 9507546 A	05-08-1997
			CA 2188649 A1	02-11-1995
			CN 1151128 A	04-06-1997
			CZ 9603097 A3	17-09-1997
			EP 0757589 A1	12-02-1997
			FI 964305 A	23-12-1996
			HU 75287 A2	28-05-1997
			JP 3100638 B2	16-10-2000
			JP 9511948 T	02-12-1997
			LT 96152 A ,B	26-05-1997
			LV 11791 A	20-06-1997
			NO 964536 A	25-10-1996

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 01/19952

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5547760	A	NZ 284360 A	26-01-1998
		PL 317023 A1	03-03-1997
		WO 9529008 A1	02-11-1995
		US 5618433 A	08-04-1997
		US 5980987 A	09-11-1999
		US 2001021413 A1	13-09-2001
EP 0045824	A	17-02-1982	EP 0045824 A1
			17-02-1982